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Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1971), 48(6): 249-263
Issue Date	1971-03-24
URL	<a href="http://hdl.handle.net/2433/76349">http://hdl.handle.net/2433/76349</a>
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

## Infrared Absorption Spectra of Tetracyanoethylene Adsorbed on Evaporated Alkali Halides

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*Received October 21, 1970*

The infrared absorption studies have been made of TCNE adsorbed on alkali halide films such as NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, and CsI at various temperatures from  $-78^{\circ}\text{C}$  to room temperatures. The films were prepared in a specially designed low-temperature cell by the method of Kozirovski and Folman for obtaining high surface area samples. It is observed that the intense bands in the spectrum of the TCNE crystal split into two components in the spectra of TCNE adsorbed at  $-78^{\circ}\text{C}$ . The relative intensity of the two components changes with the sort of alkali halides, surface coverage and temperature. This may suggest that there are two different species of physical adsorption at lower temperatures. The frequency shifts of the  $\text{C}\equiv\text{N}$  stretching vibrations were calculated for the two probable forms of adsorption by using the perturbation method. The theoretical values thus obtained are in reasonable agreement with the observed values, showing that the  $\text{C}\equiv\text{N}$  stretching force constant of TCNE is slightly increased by adsorption. A cause for this increment was discussed. The studies were also made on the effect of amine vapor on physically adsorbed TCNE. It is also found that TCNE is chemisorbed in the form of the anion radical on alkali iodide films at room temperatures.

### INTRODUCTION

Fully conjugated cyano-compounds such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) are well known as strong electron acceptors in the charge-transfer complexes. Moreover, Uyeda, Kobayashi, and Suito<sup>1)</sup> have found that TCNQ makes an epitaxial growth on the surface of the single crystal of alkali halides. In this case, the first monomolecular layer directly adsorbed on the substrates may play an important role in the orientation of the TCNQ crystal. It is therefore worth studying the adsorption of such compounds on the alkali halide surface and discussing the adsorption form as well as the adsorption force.

On the other hand, detailed studies of the vibrational spectra of TCNE have been reported by Takenaka and Hayashi<sup>2)</sup> and others.<sup>3~7)</sup> Consequently, the major spectral

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features from 3300 to 100  $\text{cm}^{-1}$  can be assigned with some confidence.\*<sup>1)</sup>

In the present work, the infrared absorption studies were made of TCNE adsorbed on alkali halide films such as NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, and CsI, which were deposited on a KBr window by the method of Kozirovski and Folman<sup>9)</sup> for obtaining high surface area films. The results obtained were discussed with the aid of the spectral assignments given for the free TCNE molecule.<sup>2)</sup> The frequency shifts of the  $\text{C}\equiv\text{N}$  stretching vibrations were calculated for two different forms of physically adsorbed TCNE by using the perturbation method.<sup>10)</sup>

## EXPERIMENTAL

### 1. Apparatus.

The adsorbent films of alkali halides were prepared in a low-temperature infrared cell illustrated in Fig. 1. It was essentially the same as that designed by Wagner and Hornig,<sup>11)</sup> except for a furnace compartment for evaporation of alkali halides and a sample container. The cell was made of glass, being composed of two main parts: one was the vacuum jacket A having the furnace compartment F as well as the sample container S on its each side, and the other consisted of the Dewar B and the copper frame E. Both parts were jointed together by means of the ground joint C. Two KBr windows were vacuum-sealed onto the flat ground ends of A with a glyptal resin. The windows  $W_1$  and  $W_2$  were 50 and 40 mm diameter, respectively. In the case of infrared measurements, the larger window was directed towards the light source in order to allow as much radiation as possible to be transmitted through the cell. The sample container S was connected to the inside of A through a tap  $T_2$ . A tungsten coil H was led into F by means of a tungsten-glass seal and a ground joint D. The copper frame E was directly attached to the Dewar by using a Kover seal. The inner KBr window  $W_3$ , on which the alkali halides were deposited, was placed inside the frame. The temperatures of the adsorbent films and the furnace were separately measured by means of two pairs of thermocouple leads  $G_1$  and  $G_2$ . The cell was connected to the vacuum system through a main tap  $T_1$  and a ball joint K.

The infrared spectra of adsorbed TCNE were recorded from 4000 to 400  $\text{cm}^{-1}$  with the aid of a Perkin-Elmer model 521 grating spectrometer. A 10-cm gas cell was placed in the reference beam of the spectrometer for compensation of atmospheric absorptions. The calibration of the spectrometer was carried out by using indene, polystyrene, and atmospheric water,<sup>12)</sup> and the error of the wavenumber measurements was estimated to be 0.5  $\text{cm}^{-1}$ .

### 2. Materials.

The adsorbent films of NaCl, NaBr, KCl, and KBr were prepared from single crystals grown by the Kyropoulos method,<sup>13)</sup> whereas those of NaI, KI, CsCl, and CsI

\*1 Takenaka and Hayashi<sup>2)</sup> gave a reverse assignment of the  $A_g$  and  $B_{1g}$   $\text{C}\equiv\text{N}$  stretching modes compared to that presented in references 4), 5), and 6). However, their assignment was supported by the calculations in reference 5) and a current work with charge-transfer complexes of TCNE.<sup>8)</sup>

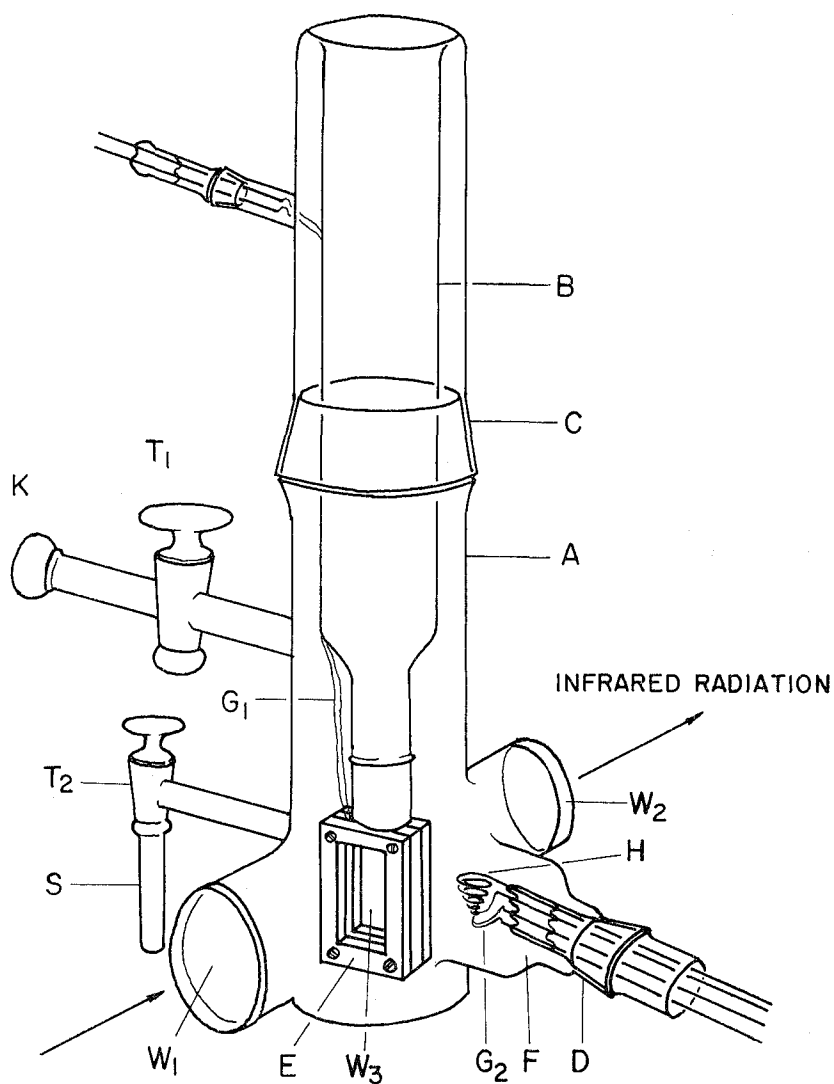


Fig. 1. Low-temperature adsorption cell for infrared measurements.

from analytical grade crystals. TCNE was reagent grade chemicals and purified by repeated sublimations at atmospheric pressure.

### 3. Procedure.

A small amount of TCNE was placed in the sample container and a small crystal of alkali halide (*ca.* 0.3 g) inside the tungsten coil. The cell was assembled so that the inner window  $W_3$  faced the heater H, and connected to the vacuum system. After several hours of evacuation at  $10^{-6}$  mmHg, the crystal was gradually heated up to *ca.* 400°C and kept at this temperature for 30 minutes in order to remove traces of water and other volatile impurities. The deposition of alkali halides was carried out keeping the

inner window either at room temperatures or at  $-78^{\circ}\text{C}$ . In the latter case, dry-ice was slowly introduced into acetone in the Dewar so that the inner window was cooled gradually to prevent cracking. The salt was evaporated by heating the furnace after the manner of Kozirovski and Folman,<sup>9)</sup> who have suggested that the film thus prepared have specific surface area greater than *ca.*  $200\text{ m}^2/\text{g}$ . Then, the inner window  $W_3$  was turned by  $90^{\circ}$  with the aid of the ground joint C in order to make  $W_3$  parallel to the outer windows  $W_1$  and  $W_2$  for infrared measurements. After one hour of evacuation at  $10^{-6}\text{ mmHg}$ , TCNE was slowly heated up to *ca.*  $70^{\circ}\text{C}$  and kept at this temperature while it was adsorbed on the alkali halide film cooled to  $-78^{\circ}\text{C}$ . The amount of adsorbed TCNE was restricted less than that of monolayer coverage, which was estimated from the cross-sectional area of the TCNE molecule and the surface area of alkali halide.

## RESULTS AND DISCUSSION

Neither absorption nor scattering of radiation were observed through the region from  $4000$  to  $400\text{ cm}^{-1}$  after film deposition. It may suggest the absence of adsorbed water on alkali halide films and the possibility of having obtained high surface area films as stated by Kozirovski and Folman.<sup>9)</sup>

### 1. Spectra of TCNE on NaCl, NaBr, KCl, KBr, and CsCl.

The infrared absorption spectra of TCNE adsorbed on NaCl, NaBr, KCl, and KBr films at  $-78^{\circ}\text{C}$  are shown in Fig. 2, together with that of the TCNE crystal for reference. The spectrum of TCNE adsorbed on CsCl film was almost the same as that on NaCl film. It is found from Fig. 2D that all the very intense bands observed in the spectrum of the TCNE crystal split into two components in the spectrum of TCNE adsorbed on KCl film, except for a  $959\text{ cm}^{-1}$  band where no indication of splitting is found. Figure 3 gives the intensity changes of the splitting bands due to the changes of surface coverage and temperature. When the surface coverage was increased at  $-78^{\circ}\text{C}$  (Fig. 3B), one component (indicated by *b* in Fig. 3) of the splitting bands increased its intensity more rapidly as compared with the other component (indicated by *a* in Fig. 3). When the temperature was raised to *ca.*  $-30^{\circ}\text{C}$  (Fig. 3C), the *a*-component decreased its intensity but the *b*-component increased slightly. When the temperature was raised further to room temperatures (Fig. 3D), the intensity of the *a*-component remained constant first, and that of the *b*-component decreased very rapidly. After the *b*-component disappeared, the *a*-component weakened slowly until it finally disappeared. The same phenomena of the band splitting (Fig. 2E) and the intensity change were also found in the spectrum of TCNE adsorbed on KBr film. Thus it is apparent that the components of the splitting bands can be classified into two groups *a* and *b*, which behave independently upon adsorption and desorption. This suggests that there are two different adsorbed species of TCNE on these films. The *a*- and *b*-components of the  $959\text{ cm}^{-1}$  band are thought to fall to the same frequency, providing no frequency shift from that of the TCNE crystal.

In the spectrum of TCNE adsorbed on NaCl (Fig. 2B) or CsCl, the *a*-components

# Infrared Spectra of Adsorbed TCNE

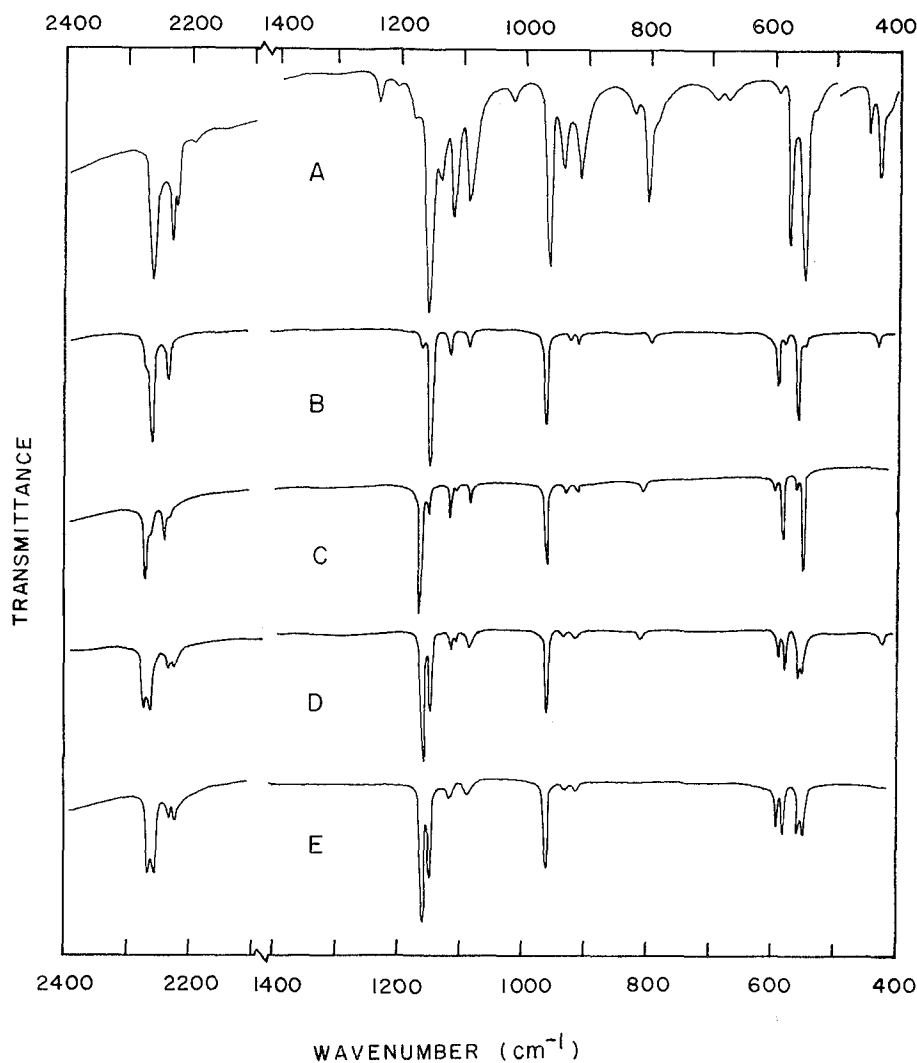
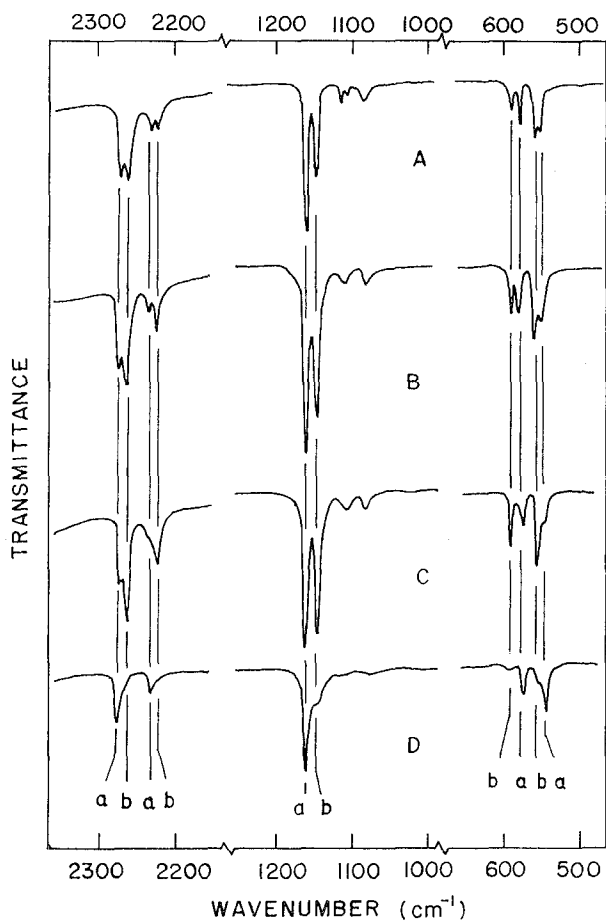


Fig. 2. Infrared spectra of (A) TCNE crystal and TCNE adsorbed on (B) NaCl, (C) NaBr, (D) KCl and (E) KBr films at  $-78^{\circ}\text{C}$ .

of all the splitting bands appeared as weak shoulders or traces, whereas the *b*-components as definite bands. In the spectrum of TCNE adsorbed on NaBr (Fig. 2C), on the other hand, the *a*-components appeared as definite bands, whereas the *b*-components as weak shoulders or traces. In Table 1, are summarized the frequencies of adsorbed TCNE on NaCl, NaBr, KCl KBr, and CsCl films at  $-78^{\circ}\text{C}$  and their classifications into the *a*- and *b*-groups. The weaker bands in the solid phase spectra could not be divided into the two groups in the adsorption spectra, since all the components of the splitting bands were not necessarily detectable. It is clear from Table 1 that the frequencies of all the adsorbate bands are nearly constant irrespective of the sort of alkali halides used as adsorbents. In Table 2, the mean values of the frequencies



- (A)  $-78^\circ\text{C}$ , lower coverage.
- (B)  $-78^\circ\text{C}$ , higher coverage.
- (C)  $-30^\circ\text{C}$ .
- (D) immediately after temperature is raised to  $23^\circ\text{C}$ .

Fig. 3. Infrared spectra of TCNE adsorbed on KCl film.

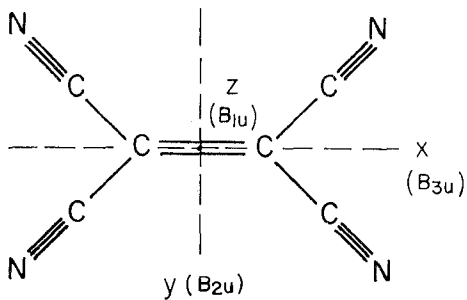


Fig. 4. The molecular-fixed axes of TCNE ( $D_{2h} \equiv V_h$ ).

# Infrared Spectra of Adsorbed TCNE

Table 1. Infrared Frequencies ( $\text{cm}^{-1}$ ) of TCNE Adsorbed on Various Alkali Halides at  $-78^\circ\text{C}$ .

TCNE crystal	TCNE adsorbed on								Component
	NaCl	NaBr	NaI	KCl	KBr	KI	CsCl	CsI	
2262 m	2266 sh	2267 m	2266 m	2266 m	2267 m	2266 m	2266 sh	2266 m	<i>a</i>
	2262 m	2262 sh	2262 sh	2262 m	2263 m	2258 sh	2262 m	2262 m	<i>b</i>
2230 m	2222 w	2232 w	2231 w	2232 w	2232 w	2230 w		2232 w	<i>a</i>
		2222 sh	2223 sh	2222 w	2223 w	2223 sh	2222 w	2222 w	<i>b</i>
1155 s	1155 sh	1155 m	1155 m	1155 m	1155 m	1157 m	1155 sh	1156 m	<i>a</i>
	1147 m	1147 sh	1146 w	1146 m	1146 m		1148 m	1147 m	<i>b</i>
1115 m		1117 w	1116 w	1115 w	1116 w	1118 w		1118 w	
	1113 w	1113 vw		1112 vw			1114 w	1115 vw	
1086 m	1089 w	1088 w	1087 w	1086 w	1088 w	1089 w	1190 w	1088 w	
959 s	959 m	959 m	959 m	959 m	959 m	961 m	960 m	960 m	<i>a</i> and <i>b</i>
935 m	925 vw	934 vw	935 vw	934 vw	934 vw	935 vw	925 vw	935 vw	
916 m	915 vw	915 vw	915 vw	915 vw	915 vw	918 vw	914 vw	915 vw	
804 m	789 vw	804 vw	804 vw	802 vw		804 vw	797 vw		
579 s	591 m	592 sh	590 vw	590 w	590 w		592 m	591 w	<i>b</i>
	580 vw	581 m	579 m	580 w	580 w	580 m	580 vw	581 w	<i>a</i>
555 s	561 m	561 sh	559 sh	560 w	559 w		560 m	561 w	<i>b</i>
	557 sh	558 m	555 m	557 w	556 w	556 m		557 w	<i>a</i>
429 m	427 vw			425 vw			427 vw		

Table 2. Comparison of Infrared Frequencies of TCNE between Crystal and Adsorbed Species.

TCNE crystal			<i>a</i> -Component		<i>b</i> -Component	
Freq. ( $\text{cm}^{-1}$ )	Sym. species	Assignment	Freq. ( $\text{cm}^{-1}$ )	Freq. shift ( $\text{cm}^{-1}$ )	Freq. ( $\text{cm}^{-1}$ )	Freq. shift ( $\text{cm}^{-1}$ )
2262	$B_{3u}$	$\text{C}\equiv\text{N}$ stretch.	2266	+4	2262	0
2230	$B_{2u}$	$\text{C}\equiv\text{N}$ stretch.	2232	+2	2222	-8
1155	$B_{2u}$	$\text{C}-\text{C}$ stretch.	1155	0	1147	-8
959	$B_{3u}$	$\text{C}-\text{C}$ stretch.	959	0	959	0
579	$B_{3u}$	$\text{C}-\text{C}-\text{C}$ bend.	580	+1	591	+12
555	$B_{1u}$	$\text{C}-\text{C}-\text{C}$ wag.	557	+2	560	+5

of the *a*- and *b*-components are compared with those of the TCNE crystal which has been studied in the previous work.<sup>2)</sup> According to the group theoretical considerations, the infrared-active, in-plane vibrations of the TCNE molecule ( $D_{2h} \equiv V_h$  symmetry) are divided into two symmetry species  $B_{2u}$  and  $B_{3u}$ , which have transition moments parallel to the  $y$ - and  $x$ -axes, respectively (Fig. 4). The infrared-active, out-of-plane vibrations belong to the  $B_{1u}$  symmetry species, having transition moments parallel to the  $z$ -axis. The symmetry species and assignments of the frequencies of the TCNE crystal are also given in Table 2.

It is seen from Table 2 that the *a*-components of both the two  $\text{C}\equiv\text{N}$  stretching vibrations belonging to the  $B_{2u}$  and  $B_{3u}$  symmetry species are slightly shifted towards higher frequencies upon adsorption, and the *a*-components of both the two  $\text{C}-\text{C}$  stretch-



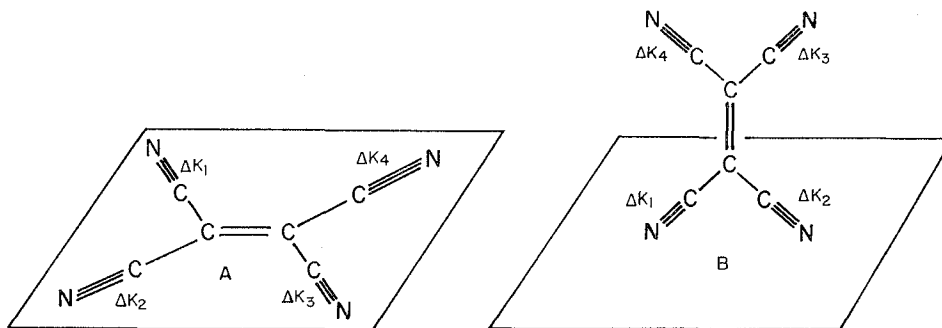


Fig. 5. Two probable forms of physically adsorbed TCNE on alkali halides.

ing vibrations belonging to the  $B_{2u}$  and  $B_{3u}$  symmetry species remain unchanged from the frequencies of the TCNE crystal. In other words, the frequency shifts of the  $a$ -components are nearly the same for the two  $C\equiv N$  stretching vibrations belonging to the  $B_{2u}$  and  $B_{3u}$  symmetry species, and it is also true for the two  $C-C$  stretching vibrations belonging to these symmetry species. It is therefore likely that the absorption bands of the  $a$ -component arise from TCNE adsorbed in the form illustrated in Fig. 5A, because in this case the  $x$ - and  $y$ -axes of the TCNE molecule may be perturbed by the same magnitude from the alkali halide surface.

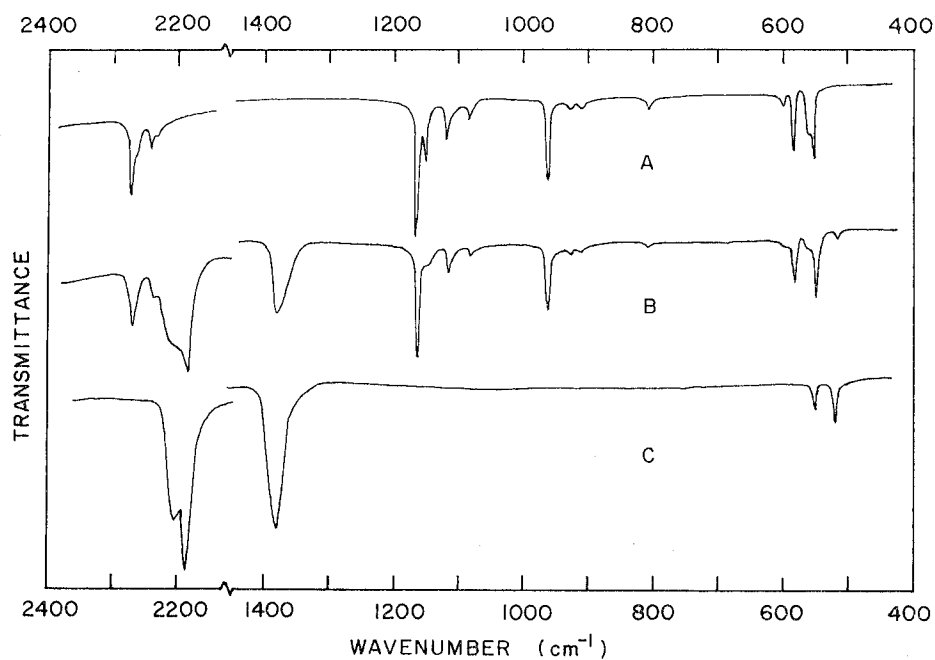
On the other hand, the  $b$ -components of the  $C\equiv N$  and the  $C-C$  stretching vibrations belonging to the  $B_{2u}$  symmetry species are shifted by  $8\text{ cm}^{-1}$  towards lower frequencies upon adsorption, whereas those belonging to the  $B_{3u}$  symmetry species remain unchanged from the frequencies of the TCNE crystal. This may suggest that the perturbation of the alkali halide surface is much larger upon the stretching modes having the transition moments parallel to the  $y$ -axis than upon those having the transition moments parallel to the  $x$ -axis. It is therefore conceivable that the absorption bands of the  $b$ -component arise from TCNE adsorbed in the form illustrated in Fig. 5B, because in this case the  $C_2$  symmetry about the  $x$ -axis in the free molecule is kept in the adsorbed species whereas that about the  $y$ -axis vanishes. In the latter part of the present paper, the frequency shifts of the  $C\equiv N$  stretching modes due to adsorption will be discussed quantitatively under the assumption of the adsorption forms given in Figs. 5A and 5B by using the perturbation method.<sup>10)</sup>

Since, as mentioned above, all the absorption bands disappeared within 2 or 3 hours after temperature was raised to room temperatures, it may be concluded that TCNE is physically adsorbed on NaCl, NaBr, KCl, KBr, and CsCl films at  $-78^\circ\text{C}$ , but desorbed at higher temperatures.

## 2. Spectra of TCNE on NaI, KI, and CsI.

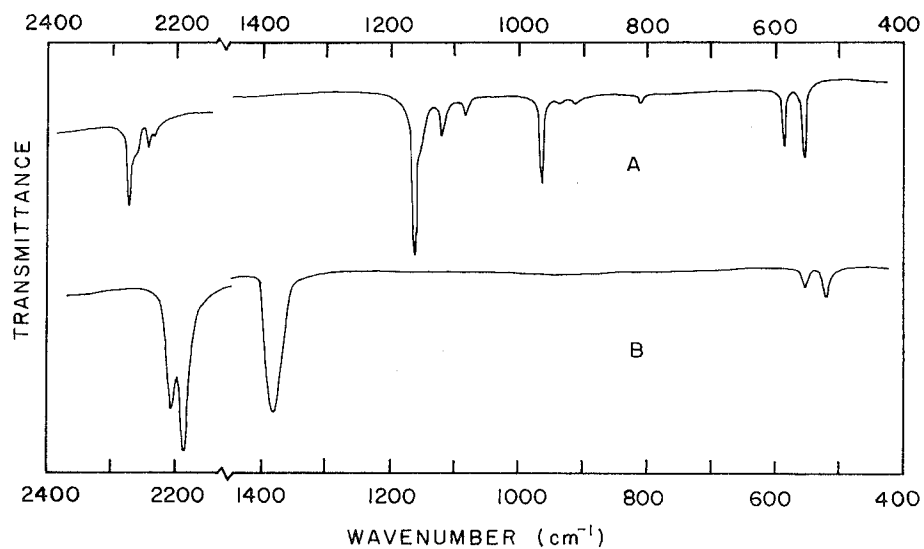
Figures 6-8 represent the infrared spectra of TCNE adsorbed on NaI, KI and CsI films, respectively, at  $-78^\circ\text{C}$  as well as room temperatures. The spectra of TCNE adsorbed on NaI (Fig. 6A) and KI films (Fig. 7A) at  $-78^\circ\text{C}$  bore a close resemblance to that on NaBr (Fig. 2C), where the  $a$ -components appeared as definite bands and the  $b$ -components as weak shoulders or traces. The spectrum of TCNE adsorbed on

# Infrared Spectra of Adsorbed TCNE



- (A) -78°C.
- (B) 30 min. after temperature is raised to 23°C.
- (C) 90 min. after temperature is raised to 23°C.

Fig. 6. Infrared spectra of TCNE adsorbed on NaI film.



- (A) -78°C.
- (B) 90 min. after temperature is raised to 23°C.

Fig. 7. Infrared spectra of TCNE adsorbed on KI film.

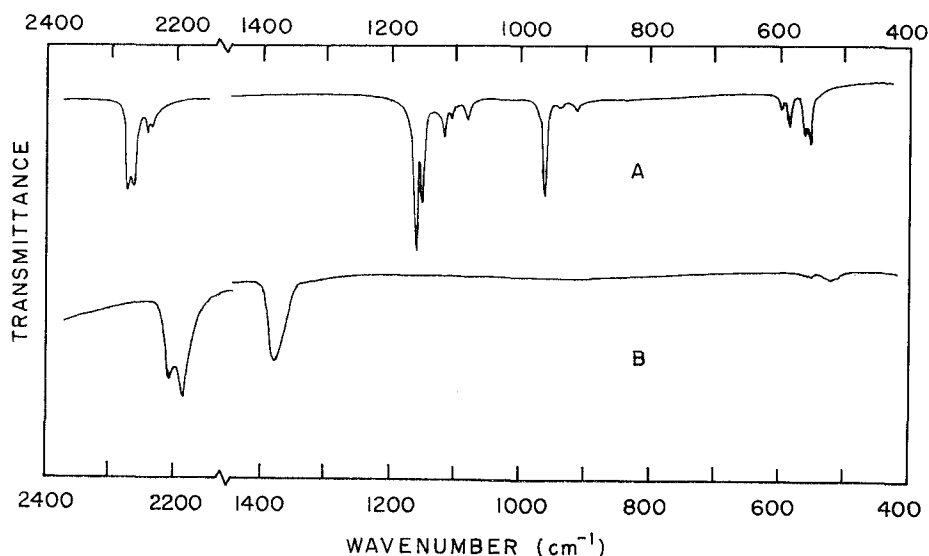
(A)  $-78^{\circ}\text{C}$ .(B) 90 min. after temperature is raised to  $23^{\circ}\text{C}$ .

Fig. 8. Infrared spectra of TCNE adsorbed on CaI film.

CsI film at  $-78^{\circ}\text{C}$  (Fig. 8A) was nearly the same as that on KCl and KBr films (Figs. 2D and 2E, respectively), where the *a*- and *b*-components appeared as the splitting bands of nearly the same intensities. The observed frequencies of TCNE adsorbed on alkali iodide films at  $-78^{\circ}\text{C}$  are also given in Table 2.

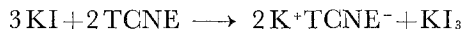
A large difference of the spectra was found at room temperatures between TCNE adsorbed on alkali iodides and that on the other alkali halides. When the temperature was raised to *ca.*  $0^{\circ}\text{C}$ , the gradual change in the relative intensities of the *a*- and *b*-components was observed in the spectrum of TCNE adsorbed on alkali iodides. When the temperature was raised further to room temperatures (Fig. 6B), some new bands started to appear, and after the following 90 minutes, the spectrum attained to the final one (Figs. 6C, 7B, and 8B) which was entirely different from the initial one. The frequencies of the final spectra are listed in Table 3. They are the same as that of the TCNE anion radical ( $\text{TCNE}^-$ ) reported by Stanley *et al.*<sup>8)</sup>. They have assigned very

Table 3. Infrared Frequencies ( $\text{cm}^{-1}$ ) of TCNE Adsorbed on Alkali Iodides at Room Temperatures.

NaI	KI	CsI
2206 s	2204 m	2196 s
2184 s	2185 s	2172 s
1389 s	1368 s	1352 s
556 w	552 w	
524 w	522 w	

intense bands of  $\text{TCNE}^-$  at *ca.* 2200 and 1371  $\text{cm}^{-1}$  to the totally symmetric  $\text{C}\equiv\text{N}$  and  $\text{C}=\text{C}$  stretching modes, respectively, which are activated in the infrared spectrum by a strong charge-transfer interaction or a distortion of the electron cloud.<sup>\*2)</sup> It may therefore be concluded that TCNE is physically adsorbed on alkali iodides at  $-78^\circ\text{C}$  but chemisorbed in the form of  $\text{TCNE}^-$  at room temperatures.

Webster *et al.*<sup>14)</sup> have reported that the reaction of TCNE with potassium iodide



provides a convenient laboratory synthesis of  $\text{TCNE}^-$ , and that  $\text{K}^+\text{TCNE}^-$  is stable to usual atmospheric conditions for several weeks. In the present study, the similar reaction may be accomplished on the surface of alkali iodides.

### 3. Effect of amine vapor on physically adsorbed TCNE

Addition of a small amount of amine vapor to the physically adsorbed TCNE on alkali halides gave a marked spectral change. Figure 9 shows the infrared spectrum of TCNE which is adsorbed on KCl film at  $-78^\circ\text{C}$  and then exposed to propylamine vapor (pressure 6.2 mmHg). New intense bands appeared at 2200 and 1560  $\text{cm}^{-1}$  besides the bands of TCNE adsorbed on KCl without amine vapor. Since these bands are not observed in the spectrum of propylamine vapor, they are ascribed to new species formed on the KCl surface by the addition of propylamine. The same bands have been found by Stanley *et al.*<sup>8)</sup> on the formation of weak charge-transfer complexes TCNE-hexamethylbenzene and TCNE-pentamethylbenzene. They have assigned those bands to the totally symmetric  $\text{C}\equiv\text{N}$  and  $\text{C}=\text{C}$  stretching modes of partially ionized TCNE, which may be activated in the infrared spectrum by virtue of the influence of the donor modes on the vertical ionization potential or electron affinity of the acceptor molecule in the planar sandwich complexes. Thus it may be concluded

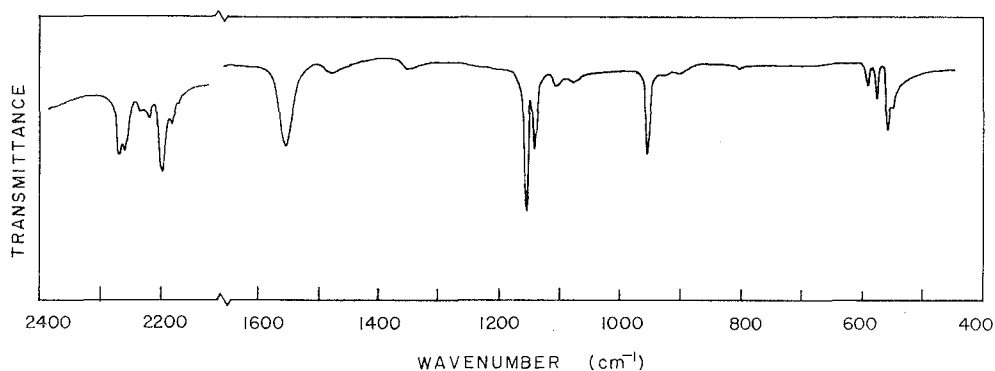


Fig. 9. Infrared spectra of TCNE adsorbed on KCl film at  $-78^\circ\text{C}$  and then exposed to propylamine vapor (6.2 mmHg).

\*2 The totally symmetric  $\text{C}\equiv\text{N}$  and  $\text{C}=\text{C}$  stretching modes of the neutral TCNE molecule have been found at 2250 and 1573  $\text{cm}^{-1}$ , respectively, in the Raman spectrum of the crystal<sup>2)</sup>.

that propylamine forms weak charge-transfer complex with TCNE on the alkali halide surface at  $-78^{\circ}\text{C}$ .

When a small amount of triethylamine was added to physically adsorbed TCNE on NaCl or KCl film, no change of the spectrum was observed at  $-78^{\circ}\text{C}$ . However, when the sample was warmed up to room temperatures, new intense bands appeared at 2202, 2197, 2178, 2168, and  $1370\text{ cm}^{-1}$ . Since those frequencies are the same as those of  $\text{TCNE}^-$  as mentioned above, it may be obvious that triethylamine forms the TCNE anion salt on the alkali halide surface at room temperatures.

### CALCULATION OF SPECTRAL SHIFTS

In the previous section, it is suggested that the splitting bands of TCNE physically adsorbed on the alkali halide films at  $-78^{\circ}\text{C}$  are classified into the *a*- and *b*-groups, and that the absorption bands of the *a*- and *b*-groups arise respectively from the adsorbed species illustrated in Figs. 5A and 5B. In this section, the frequency shifts of the  $\text{C}\equiv\text{N}$  stretching vibrations caused by the transition from the vapor phase to the adsorbed species A and B are calculated by the aid of the **GF** matrix method<sup>10)</sup> taking the perturbation of the surface on the  $\text{C}\equiv\text{N}$  stretching force constants into account. In the calculation, the vibration bands at *ca.*  $2250\text{ cm}^{-1}$  are assumed to be pure  $\text{C}\equiv\text{N}$  stretching modes in spite of the result of the previous paper<sup>2)</sup> that *ca.* 85% of their potential energies is distributed to the  $\text{C}\equiv\text{N}$  stretching modes and the remains to the  $\text{C}-\text{C}$  stretching modes.

According to the **GF** matrix method, the diagonal matrix  $\mathbf{A}^0$  whose elements are the characteristic values ( $\lambda_1^0, \lambda_2^0, \dots$ ) of the  $\mathbf{G}^0\mathbf{F}^0$  matrix is given by

$$\mathbf{A}^0 = \tilde{\mathbf{L}}^0\mathbf{F}^0\mathbf{L}^0. \quad (1)$$

Here,  $\mathbf{F}^0$  is the potential energy matrix in terms of the internal symmetry coordinates,  $\mathbf{L}^0$  the matrix whose columns are the characteristic vectors of the  $\mathbf{G}^0\mathbf{F}^0$  matrix, and  $\tilde{\mathbf{L}}^0$  the transpose of the  $\mathbf{L}^0$  matrix. The superscript 0 refers to the free TCNE molecule.

If the  $\text{C}\equiv\text{N}$  stretching force constants are perturbed by a small amount  $\Delta\mathbf{F}$  by adsorption of TCNE on alkali halides, we have

$$\mathbf{A} = \tilde{\mathbf{L}}\tilde{\mathbf{L}}^0(\mathbf{F}^0 + \Delta\mathbf{F})\mathbf{L}^0\mathbf{L}, \quad (2)$$

where  $\mathbf{L}$  is the matrix for transforming  $\tilde{\mathbf{L}}^0(\mathbf{F}^0 + \Delta\mathbf{F})\mathbf{L}^0$  into the diagonal matrix  $\mathbf{A}$ , whose elements are characteristic values ( $\lambda_1, \lambda_2, \dots$ ) of the **GF** matrix of adsorbed TCNE. Then the secular determinant for the perturbed molecule has the form

$$|\tilde{\mathbf{L}}^0(\mathbf{F}^0 + \Delta\mathbf{F})\mathbf{L}^0 - \lambda\mathbf{E}| = 0, \quad (3)$$

where  $\mathbf{E}$  is the unit matrix. Using Eq. (1), we have

$$|\mathbf{A}^0 + \tilde{\mathbf{L}}^0\Delta\mathbf{F}\mathbf{L}^0 - \lambda\mathbf{E}| = 0, \quad (4)$$

and then

$$|\tilde{\mathbf{L}}^0\Delta\mathbf{F}\mathbf{L}^0 - (\lambda - \lambda^0)\mathbf{E}| = 0. \quad (5)$$

Non-zero elements of the  $\Delta\mathbf{F}$  matrix are written as follows;

$$\left. \begin{aligned} \Delta F_{3,3} = \Delta F_{7,7} = \Delta F_{11,11} = \Delta F_{15,15} &= \frac{1}{4}(\Delta K_1 + \Delta K_2 + \Delta K_3 + \Delta K_4) \\ \Delta F_{3,7} = \Delta F_{11,15} &= \frac{1}{4}(\Delta K_1 - \Delta K_2 + \Delta K_3 - \Delta K_4) \\ \Delta F_{3,15} = \Delta F_{7,11} &= \frac{1}{4}(\Delta K_1 + \Delta K_2 - \Delta K_3 - \Delta K_4) \\ \Delta F_{3,11} = \Delta F_{7,15} &= \frac{1}{4}(\Delta K_1 - \Delta K_2 - \Delta K_3 + \Delta K_4) \end{aligned} \right\} \quad (6)$$

Here  $\Delta F_{i,j}$  is the element of the  $\Delta F$  matrix concerning the internal symmetry coordinates  $S_i$  and  $S_j$ . The coordinates  $S_3$ ,  $S_7$ ,  $S_{11}$ , and  $S_{15}$  represent the  $C \equiv N$  stretching modes belonging to the  $A_g$ ,  $B_{1g}$ ,  $B_{2u}$ , and  $B_{3u}$  symmetry species, respectively, as given in Table II of the previous paper<sup>21</sup>.  $\Delta K_1$ ,  $\Delta K_2$ ,  $\Delta K_3$  and  $\Delta K_4$  are the changes of the  $C \equiv N$  stretching force constant  $K(C \equiv N)$  as shown in Fig. 5. The  $L^0$  matrix used here is that calculated in the previous study<sup>21</sup> for free TCNE molecule.

In the case of the adsorbed species A, it seems reasonable to assume  $\Delta K_1 = \Delta K_2 = \Delta K_3 = \Delta K_4 \equiv \Delta K_A$  and then Eq. (5) is reduced to the simple forms

$$0.0860 \Delta K_A - (\lambda - \lambda^0)_{B_{2u}} = 0 \quad (7)$$

and

$$0.1504 \Delta K_A - (\lambda - \lambda^0)_{B_{3u}} = 0 \quad (8)$$

for the infrared-active symmetry species  $B_{2u}$  and  $B_{3u}$ . Using a well-known relation between  $\lambda$  and the wavenumber  $\nu$

$$\nu = \sqrt{\lambda} / 2\pi c \quad (9)$$

and the observed frequencies in the vapor phase<sup>21</sup>

$$\nu_{B_{2u}}^0 = 2217 \text{ cm}^{-1} \quad \text{and} \quad \nu_{B_{3u}}^0 = 2248 \text{ cm}^{-1},$$

we have

$$\nu_{B_{2u}}(\text{calc}) = 2230 \text{ cm}^{-1} \quad \text{and} \quad \nu_{B_{3u}}(\text{calc}) = 2268 \text{ cm}^{-1}$$

as the frequencies of adsorbed TCNE, under the assumption of

$$\Delta K_A = 0.37 \text{ mdyne/\AA}.$$

These frequencies are in reasonable agreement with the observed values given in Table 2, *i.e.*,

$$\nu_{B_{2u}}(\text{obs}) = 2232 \text{ cm}^{-1} \quad \text{and} \quad \nu_{B_{3u}}(\text{obs}) = 2266 \text{ cm}^{-1}.$$

In the case of the adsorbed species B, on the other hand,  $\Delta K_1 = \Delta K_2 \equiv \Delta K_B$  and  $\Delta K_3 = \Delta K_4 = 0$ , and then Eq. (5) is reduced to the forms

$$\begin{vmatrix} 0.0756 \Delta K_B - (\lambda - \lambda^0)_{A_g} & 0.0754 \Delta K_B \\ 0.0754 \Delta K_B & 0.0752 \Delta K_B - (\lambda - \lambda^0)_{B_{3u}} \end{vmatrix} = 0 \quad (10)$$

and

$$\begin{vmatrix} 0.0742 \Delta K_B - (\lambda - \lambda^0)_{B_{1g}} & 0.0565 \Delta K_B \\ 0.0565 \Delta K_B & 0.0430 \Delta K_B - (\lambda - \lambda^0)_{B_{2u}} \end{vmatrix} = 0 \quad (11)$$

indicating the coupling between the  $A_g$  and  $B_{3u}$  frequencies and that between the  $B_{1g}$  and  $B_{2u}$  frequencies. In the calculation of Eqs. (10) and (11), the values of  $\lambda_{A_g}^0$  and  $\lambda_{B_{1g}}^0$  are necessary besides those of  $\lambda_{B_{2u}}^0$  and  $\lambda_{B_{3u}}^0$ . Since no Raman spectrum has been recorded in the vapor phase yet, we assumed the Raman frequencies

$$\nu_{A_g}^0 = 2235 \text{ cm}^{-1} \quad \text{and} \quad \nu_{B_{1g}}^0 = 2223 \text{ cm}^{-1},$$

by reference to the frequency difference in the infrared-active  $\text{C}\equiv\text{N}$  stretching vibrations between the vapor phase and the solid phase, and to the frequencies of the Raman-active vibrations in the solid phase. Thus the frequencies of the infrared-active vibrations of adsorbed TCNE are calculated as

$$\nu_{B_{2u}}(\text{calc}) = 2221 \text{ cm}^{-1} \quad \text{and} \quad \nu_{B_{3u}}(\text{calc}) = 2262 \text{ cm}^{-1},$$

by using

$$\Delta K_B = 0.031 \text{ mdyne/\AA}.$$

These frequencies are in good agreement with the observed values given in Table 2, *i.e.*,

$$\nu_{B_{2u}}(\text{obs}) = 2222 \text{ cm}^{-1} \quad \text{and} \quad \nu_{B_{3u}}(\text{obs}) = 2262 \text{ cm}^{-1}.$$

It is noteworthy that the perturbation of the alkali halide surface upon the  $\text{C}\equiv\text{N}$  stretching force constant of adsorbed TCNE is nearly constant irrespective of adsorbed species A and B. The  $\text{C}\equiv\text{N}$  stretching force constants are slightly increased by adsorption. Although it is unusual, the same increase in the  $\text{C}\equiv\text{N}$  stretching force constants has been found on complex formation between alkyl cyanide and metal halides,<sup>15)</sup> where the bondings occur through the lone pair electrons on the nitrogen atom, and has been explained by a small increase in the ionic character<sup>16)</sup> of the  $\text{C}\equiv\text{N}$  bonds.<sup>15)</sup> In the present study, the evidence for increasing polarity is provided by the intensity increase of the  $\text{C}\equiv\text{N}$  stretching modes upon adsorption. This concept of the ionic character has also been used to explain the  $\text{C}\equiv\text{N}$  stretching frequencies of inorganic and organic cyanides.<sup>17)</sup> The amount of increasing force constant  $\Delta K = 0.31 \sim 0.37$  mdyne/ $\text{\AA}$  is thought to be reasonable by referring to the fact that the force constant of the intermolecular hydrogen bonding between low-membered carboxylic acids<sup>18,19)</sup> is  $0.33 \sim 0.36$  mdyne/ $\text{\AA}$ .

#### ACKNOWLEDGMENT

The authors wish to express their gratitude to Professor Emeritus R. Gotoh and Professor E. Suito of Kyoto University for their continuing interest and encouragements during the course of this work. Thanks are also due to Dr. S. Hayashi and Dr. T. Kobayashi of the Institute for Chemical Research, Kyoto University for their valuable discussions.

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